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ScienceDirect

Procedia Engineering 120 (2015) 480 – 483

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2015

Performance evaluation of amperometric sensors for the monitoring of O_3 and NO_2 in ambient air at ppb level

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Abstract

Hereafter we present a laboratory evaluation of commercially available amperometric sensors for the monitoring of O_3 and NO_2 in ambient air at ppb level. The tests includes the determination of the response time of sensors, their calibration function, the evaluations of repeatability, short and long term drifts, the hysteresis effect and the matrix effect. Interferences from gaseous compounds, temperature and humidity parameters are also evaluated.

Peer-review under responsibility of the organizing committee of EUROSENSORS 2015

Keywords: Protocol of sensor evaluation, measurement uncertainty, low cost sensors, validation

1. Introduction

Gas sensors are identified as emerging devices for indicative measurements as defined in the European Air Quality Directive [1]. Compared to reference measurements, gas sensors would allow air pollution monitoring at lower cost. Among the types of low cost sensors for monitoring O_3 and NO_2 in ambient air, amperometric sensors are among the most suited sensors [2]. These sensors include at least a measuring and a counter electrodes. The gas molecules diffuses into the sensor and the measuring electrode where a direct electron transfer takes place due to chemical reactions. These reactions produce a current proportional to the concentration of the compound [3] following the Nernst Law. Nowadays, the amperometric sensors also includes a reference electrodes, while the trend is to add a 4th auxiliary electrode for correction of electrodes physical changes and sensor drift. Hereafter we present

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Peer-review under responsibility of the organizing committee of EUROSENSORS 2015
doi:10.1016/j.proeng.2015.08.676

an evaluation of commercially available sensors for O_3 and NO_2. The experimental design follows the Protocol of evaluation of low-cost gas sensors for air pollution [4]. Precise set up of experiments and details of the data treatment are given in this protocol. The design of experiment included the evaluation of the sensor response times, their calibration, the evaluations of their repeatability, short and long term drifts, hysteresis and matrix effect. Interferences were evaluated from gaseous compounds and temperature and humidity. All these results allow computing the laboratory sensor measurement uncertainty that can be compared with the Data Quality Objectives of the European Directive for Air Quality.

2. Experimental setup

For Alphasense (UK), the O_3 and NO_2 sensor models 03-B4 and N02-B4 were tested. The B4 type sensor is a 4-electrodes electrochemical sensor designed for ppb gas levels. The background signal of the auxiliary electrode was subtracted to the signals of the working electrode. Each sensor was mounted on a αSense test boards (αSense 4-electrodes Individual Sensor Board (ISB)).

For City Technology (UK), sensor models O3 3E1F and NO2 3E50, for O_3 and NO_2 respectively, were tested. The sensors consist of 3-electrodes amperometric sensors with organic electrolyte. These sensor were mounted on a City Technology evaluation board that converts the raw sensor signal voltage, with the possibility to vary the bias potential, using various load, feedback resistors and different levels of current amplification. The board was configured to give an output of 1V-100 nA with damping 10.

For Cairpol (F), the 3-electrodes sensor models Cairclip O3/NO2 ANA for O_3 and NO_2 and CairClip NO_2 ANA for NO_2 were tested. The CairClip sensors already include a 5V analogic output on their USB connector.

For all sensor responses, PC-powered Data Acquisition Boards (National Instrument USB 6009) were used. These boards include 4 differential analogic inputs with 14 bits analogical to digital converter. The NI USB 6009 being USB powered does not introduce a different voltage ground for power supplying and hence reduces the electronic noise in the sensor responses. The periodicity of data acquisition was 100 Hz and measurements were averaged every minute without filtering. The sensors were not calibrated by the manufacturers. A pair of each sensor models was installed inside our laboratory exposure chamber for test. The exposure chamber is described elsewhere [5]. It is able to generate gaseous mixtures and to control humidity, temperature and wind velocity. All parameters are automatically and independently set and controlled. It can accommodate several sensors for simultaneous testing. Conversely to other exposure chambers, the reference values of all compounds are measured allowing the full traceability to national/international units when evaluating sensors [5].

3. Results

The response time of sensors, t_{90}, was computed by estimating $t_{0\text{-}90}$, the time needed by the sensor to reach 90 % of the final stable value and $t_{90\text{-}0}$, the time needed to reach zero. During tests, temperature, humidity and the interfering gas compounds (e. g. NO_2 when testing O_3) were kept constant. Table 1 gives the response times of the sensors. They generally remained within 2 minutes except for the Cairclip NO_2 with filter. It is likely that the longer time response of this sensor came from the addition of an ozone filter and/or humidity buffer placed at the sensor inlet which ensured selectivity to the sole NO_2 compound. The same sensor without filter shoed a response time within 2 minutes.

The calibration levels included 90, 40, 0, 60, 20, 110 ppb for O_3 and 125, 50, 100, 0, 75, 25, 150 ppb for NO_2 in randomized order to take into account any possible hysteresis effect. Generally, calibration lines were found linear, except for one of the CairClipO3/NO2 that was unusually parabolic. Table 1 gives the coefficient of determination of the calibration lines, the standard uncertainty of lack of fit, their maximum residuals and the sensor sensitivities computed using the experimental results

The repeatability and the limit of detection of the sensors (see Table 2) were estimated by calculating the standard deviation of sensor values, s_r, with the sensor measuring at 0 and at about 100 ppb while other exposure conditions were kept constant. The repeatability of sensor was computed as $2\sqrt{2}\ s_r$ (s_r at 100 ppb) and the limit of detection was estimated as $3s_r$, (s_r at 0 ppb).

Table 1. Sensor's response time in the exposure chamber, coefficient of determination (R^2), standard uncertainty of lack of fit, maximum residual and sensitivity of sensor.

Sensors	Full scale, ppb	t_{90}	t_{0-90}	t_{90-0}	R^2	Lack of fit, ppb	Max residual, ppb	Sensitivity, mV/ppb
CairClip NO_2 (filtered)	NO_2: 90	38 min 25 s	42 min	34 min 30 s	0.9996	1.7	1.2	8.78
CairClip NO_2 (unfiltered)	O_3: 100	114 s	210 s	18 s				
NO2-B4	NO_2: 90	80 s	120 s	40 s	0.9977	1.8	3.2	0.317
NO2 3E50	NO_2: 90	98 s	128 s	68 s	0.9992	2.4	2.0	0.247
Cairclip NO_2 /O_3	O_3: 100	90 s	150 s	30 s	0.9973	2.6	1.8	7.56
O3-B4	O_3: 100	84 s	126 s	48 s	0.9998	1.5	0.5	0.161
O3 3E1F	O_3: 100	108 s	150 s	60 s	0.9986	2.2	2.8	0.485

For the short term drift, sensor responses were evaluated at 0, 60 and 90 ppb for O_3 and 0, 50, 100 and 150 ppb for NO_2 on three consecutive days, each of them being separated by a period of time between 12 and 36 hours. The mean deviations between days of the sensor responses, Dss, were calculated. The contribution to the measurement uncertainty u(Dss) was calculated using a quadratic sum of Dss and a pooled standard deviation of the Dss at all concentration levels (Table 2).

For the long term drift, a similar approach was used measuring sensor responses during 6 months about once a week. The long term drift, Dls, was estimated using the trends of the sensor responses from the beginning to the end of all experiments (150 days for O_3 and 250 days for NO_2). The standard uncertainty of the long term drift u(Dls) was estimated using the slope of the trend and the scattering of measurement around this trend (Table 2).

The effect of NO_2 for O_3 sensors and O_3 for NO_2 sensors, together with the effect of NOx, CO, CO_2 and NH_3 were evaluated at two levels. The influence of each interfering compound was determined separately. The tests were carried out at 22°C and 60 % of relative humidity and in absence of other interfering compounds. For each compound, we determined the sensitivity coefficient b and the difference of sensor responses divided by the level of the interfering compound (see Table 2). The standard uncertainty resulting from the interferents was estimated as the product of the sensitivity coefficient and the expected levels of the pollutant in background urban sites [5].

The effect of air matrix on the sensor response was tested using the calibration levels. Three different air matrixes (filtered air, ambient air and indoor air) were used for dilution. Three calibration lines were plotted, one for zero air, one for ambient air and one for indoor air and were compared. In general, all sensors showed negligible matrix effect since the calibration lines were similar.

The estimation of the dependence of sensors toward hysteresis was carried out using the calibration levels with a ramp of rising O_3 or NO_2 levels followed with a ramp of decreasing levels and finally with another rising ramp. Three calibration lines were plotted, one for the 1st ramp of rising levels, one for the falling levels and one for the 2nd ramp of rising levels. In general, the sensors showed very little hysteresis effect with only small changes of intercept values for linear lines.

Table 2. Standard deviation at 0 and 100 ppb, limit of detections (lod) and repeatability at 100 ppb(r) for sensor minutes values. The four columns on the right gives the short term drift (Dss), its standard uncertainty u(Dss) and the long term drift trend Dls with its standard uncertainty u(Dls)

Sensors	s_r (0/100 ppb)	lod, ppb	r at 100 ppb	Dss, ppb	u(Dss), ppb	Dls, ppb/days	U(Dls), ppb
CairClip NO_2 (filtered)	0.3/1.7	0.9	4.8	1.6	1.4	≤ -0.065	≤ 4.0 @ 150 ppb
NO2-B4	5.5/2.9	8.6	11.5	3.2	5.7	≤ -0.497	≤ 45 @ 150 ppb
NO2 3E50	0.15/0.8	0.5	2.3	1.2	14	≤ -0.196	≤ 7.9 @ 150 ppb
Cairclip NO_2 /O_3	-/3.3	-	9.2	1.4	1.7	≤ 0.011	≤ 1.7 @ 90 ppb
O3-B4	2.3/0.4	6.8	0.9	0.7	0.9	≤ 0.016	≤ 3.0 @ 90 ppb
O3 3E1F	0.9/0.6	2.7	1.6	1.2	1.5	≤ 0.142	≤ 5.8 @ 90 ppb

Table 3. Gaseous interfering compounds: sensitivity coefficients (ppb/ppb or ppb/ppm for CO/CO_2) / standard uncertainty in ppb. For temperature and humidity: sensitivity coefficients (°C/ppb or %/ppb) / standard uncertainty in ppb. ns: not significant

Sensors	O_3/ NO_2	NO	CO	CO_2	NH_3	Temperature	Humidity
CairClipNO_2 (filt.)	-0.010/0.3 (O_3)	-0.007/0.3	-0.001/0.5	0.009/0.3	-0.032/1.2	0.093/1.7	-0.057/2.2
NO2-B4	1.5/39 (O_3)	-3.2 10^{-2}/0.2	-1.3 10^{-3}/0.4	-4.2 10^{-2}/1.2	-8.9 10^{-2}/2.3	0.47/8.3	0.13/5.1
NO2 3E50	1.5/37 (O_3)	-0.058/0.4	-1.6 10^{-3}/0.5	-1.3 10^{-2}/0.3	-1.1 10^{-1}/2.9	0.16/2.2	0.062/2.1
CairclipNO_2/O_3	0.84/5.5 (NO_2)	0.006/0.1	0.070/0.1	-6 10^{-5}/<0.1	-1 10-2/1.0	0.24/1.9	ns/1.4
O3-B4	0.92/6.1 (NO_2)	-0.042/0.3	-0.066/0.2	2 10^{-4}/<0.1	2.5 10^{-4}/<0.1	ns/1.5	0.40/16.3
O3 3E1F	0.76/5.0 (NO_2)	-0.011/0.1	7.0 10^{-5}/0.0	3.5 10^{-3}/0.1	1.6 10^{-3}/0.1	1.3/7.4	-0.022/1.7

Finally, sensor's response are influenced by changes of temperature or relative humidity. Two series of tests were conducted independently, generating ramps of temperature and humidity in a hysteresis cycle while gaseous levels in the chamber were kept constant. The ranges of temperature changed between 12 and 32 ºC (by step of 5 ºC) and the range of humidity was kept between 40% and 80% (by step of 10%). The results of the tests are given in Table 3, including sensitivity coefficients of the sensors to temperature and humidity and the contribution of these parameters to the measurement uncertainty. The standard uncertainties include both the contribution from the sensitivity coefficients and hysteresis effect.

4. Conclusions

This laboratory evaluation shows that the O_3 and NO_2 amperometric sensors are generally found linear with a response time under 2 minutes. The limits of detection and repeatability were found both mainly under 10 ppb. Regarding gaseous interfering compounds, the experiments showed that O_3 sensors mainly suffers from NO_2 and NO_2 sensors are highly sensitive to O_3, even though these interferences would depend on the actual levels of the interferents at measurement time. NO_2 sensors seems to suffer more from long term drift than O_3 sensors and both show only a slight short term drift effect. Some huge hysteresis effect against humidity may happen while dependence on temperature may occur. For one of the NO_2 sensors, filtering of the interfering compounds together with a humidity buffer appeared to be a valid solution with the sole drawback of increasing the time response. The presented results are only valid for the version of sensors under tests in the conditions and at the time of the tests.

5. Online license transfer

Acknowledgements

This study was carried out within the EMRP Joint Research Project ENV01 MACPoll. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

References

[1] Directive 2008/50/EC of the European Parliament and the Council on ambient air quality and cleaner air for Europe, Official Journal of the European Union, vol. L 152/1, 11.6.2008.
[2] M. Aleixandre and M. Gerboles, Review of Small Commercial Sensors for Indicative Monitoring of Ambient Gas, Chemical Engineering Transactions, vol. 30, pp. 169-174, 2012.
[3] P. Jacquinot, A.W.E. Hodgson, P.C. Hauser, B. Müller, B. Wehrli, 1999. Amperometric detection of gaseous ethanol and acetaldehyde at low concentrations on an Au–Nafion electrode. Analyst 124, 871–876.
[4] L. Spinelle, M. Gerboles, M. Aleixandre, Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution, EUR 26112, Publications Office of the European Union, Luxembourg (Luxembourg), 2013
[5] L. Spinelle, M. Gerboles and A. Aleixandre, Report of laboratory and in-situ validation of micro-sensor for monitoring ambient air - Ozone micro-sensors, AlphaSense, model B4-O3 sensors (UK), EUR 26681, Publications Office of the European Union, 2014.